Proceeding Paper

Molecular Emitters as a Tunable Light Source for Optical Multisensor Systems †

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Abstract: In this study, optical multisensor systems based on molecular emitters as a light source are introduced. To obtain such light sources, cyclometalated Ir(III) complexes and Cu(I)-based complexes were synthetized and investigated. Since each complex has its own emission spectrum in the visible range, it is possible to choose an appropriate set of emitters for specific analytical tacks. The developed analytical device was successfully applied for fluoride and phosphate quantification in surface water.

Keywords: optical multisensor systems; molecular emitters; iridium complexes; copper complexes; photoluminescence; chemometrics; water analysis; fluoride; phosphate

1. Introduction

The development of portable and inexpensive analyzers allowing fast determination of the integral sample characteristics is a current trend in analytical chemistry. Optical spectroscopy in the visible and near infrared (NIR) range has a great potential due to the advances in modern optical engineering. Optical multisensor systems (OMS) are devices working on the principle of optical spectroscopy but optimized for a specific analytical task and composed of cheaper elements: light-emitting diodes (LEDs), optical fibers, 3D-printed parts, stamped optics, etc. Such specialization enables essential reduction of analyzers' price, size, and weight, thus making the analysis widely available for both real-time application and in-field measurements. There are many examples of OMS applications for various analytical problems in the recent literature [1–5].

In the present work, a novel platform for construction of OMS was suggested. The idea is to use a combination of molecular emitters as a multichannel light source with tunable intensity and wavelength range. Cyclometalated Ir(III) complexes [6] and Cu(I)-based complexes [7] were synthetized and tested in order to obtain such a light source. Each individual complex has its own emission spectrum in the visible range. This enables the selection and optimization of the light source for a specific analytical application. Several optical setup designs of OMS were developed. The proposed prototype was tested to analyze the metal ions in aqueous mixtures. The practical application of the OMS was demonstrated for the quantification of fluoride and phosphate in real surface and tap waters.

2. Methods and Materials

To obtain light sources for OMS, two sets of molecular emitters were synthesized. One of them consisted of eight cyclometalated Ir(III) compounds: firstly synthesized

[Ir(dfppy)$_2$(bpbpy)]PF$_6$ (**1**), [Ir(ppy)$_2$(bpbpy)]PF$_6$ (**2**), [Ir(pybt)$_2$(bpbpy)]PF$_6$ (**3**), and synthesized according to the standard procedure: (**4**) [8], (**5**) [9], (**6**) [10,11], (**7**) [12], and (**8**) [13]. The second set consists of six Cu(I)-based complexes: [Cu(MePPy$_3$)I]$_2$[Cu$_2$I$_4$] (**9**) [14], [Cu$_4$I$_4$(py)$_4$] (**10**) [15], [Cu(Tpdp)I] (**11**) [16], [CuCl(PPh$_3$)$_2$(py)] (**12**) [17], [Cu(PPh$_3$)$_3$(4-Mepy)]Br (**13**), and [CuI(PPh$_3$)$_2$(4-Mepy)] (**14**) [18]. The mixture of each series gives multiband light source in the region from about 400 to 800 nm.

A different optical setup was constructed for each set of emitters. A homogeneous mixture of molecular emitter powders (mixture of iridium(III) or copper(I) complexes) was placed on a glass substrate under the sample. The solution under study was placed either in a glass cup (1 cm in diameter) for the setup with Ir(III)-complexes or in a polystyrene Petri dish (3.5 cm in diameter) for the setup with Cu(I)-complexes. Initially, photoluminescence of the molecular emitters was initiated using the laser diode (λ_{exct} = 365 nm and λ_{exct} = 385 nm for the first and the second experimental setup, respectively). Further, the laser diode was replaced by a UV flashlight with λ_{exct} = 365 nm. The light that passed through the sample was recorded by a fiber-optic UV−vis spectrometer AvaSpec-ULS2048CL-EVO (Avantes, Apeldoorn, the Netherlands). The optimal geometry of the device and the required amount and placement of sample solution were chosen experimentally to obtain a stable and reproducible analytical signal.

To compare Ir(III)-based and Cu(I)-based OMS, the optical setups were tested on two separate calibration series prepared from aqueous solutions of Co(II) and Cu(II) nitrates. Each calibration set consisted of seven samples with different concentrations ranging from 0.01 to 0.1 M with a 0.015 M step for Ir(III)-based setup and ten samples with different concentrations ranging from 0.01 to 0.1 M with a 0.01 M step for Cu(I)-based setup.

The practical application of the Cu(I)-based OMS was demonstrated for quantitative determination of fluoride and phosphate in surface and tap waters. A total of 5 samples for analysis were collected from the tap, rivers, and a lake. The standard photometric methods were used as a reference for the quantification of phosphate [19] and fluoride [20] in water samples. Sample preparation for analysis was carried out in accordance with the procedures described in [19,20]. The mass concentrations of phosphate and fluoride in the calibration solutions were 0–0.96 mg/L with a 0.12 mg/L step and 0–0.4 mg/L with a 0.04 mg/L step, respectively.

To relate the analytical signal response of OMS to the analyte content, the calibration models were built using partial least-squares (PLS) regression [21]. The model performance was estimated by full cross-validation (CV) and validation with a test set. Root mean-square error (RMSE) of calibration (RMSEC), prediction (RMSEP, for the test set) or cross-validation (RMSECV) and the respective coefficients of determination (R^2) were used to compare the models.

3. Results and Discussion

In order to choose a set of appropriate emitters for multiband light sources, several requirements were established: the absorption spectrum must not overlap with the emission spectrum; excitation radiation at 365/385 nm must fit into the absorption maximum; the emission should be intense enough to be employed as the light source in the solid phase. Ir(III) luminescent complexes that have bright controlled emission fit these requirements. Another set of molecular emitters based on Cu(I) complexes is a cost-effective alternative to Ir(III) complexes and their application as a light source in OMS was also tested. The resulting mixture of each set of complexes upon excitation with the laser diode has shown emission spectra in the range of 450–800 nm (Figure 1). Emission of the mixture of eight Ir(III) compounds is higher at the right end of the spectrum from 600 to 800 nm (black line in Figure 1), while emission of the mixture of six Cu(I) complexes is higher at the left end of the spectrum (red line in Figure 1). Despite this difference, both sets are suitable as a multiband light source in the visible region.
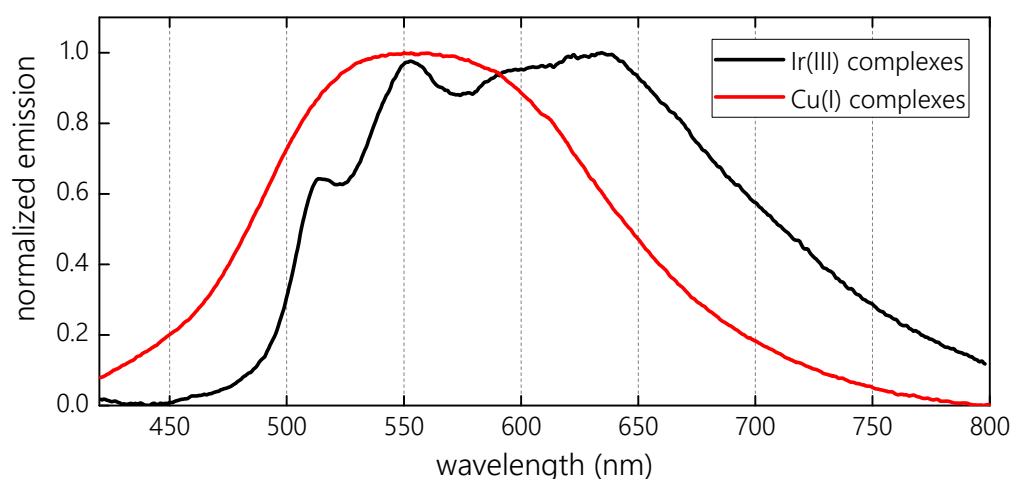
Figure 1. Normalized emission spectra of: mixture of eight Ir(III) complexes is marked in black and mixture of six Cu(I) complexes is marked in red.

The block diagram of the experimental setup is shown in Figure 2. In accordance with the proposed optical setup, the emission of molecular emitters is excited by the laser diode. The light passing through a sample is registered with a fiber-optic cable connected with a spectrometric detector. The laser diode can be replaced by inexpensive UV flashlight. Another advantage of UV flashlight is that its power is higher than that of the laser diode. Therefore, two optical setups were constructed and compared: with laser diode and with UV flashlight as excitation light.
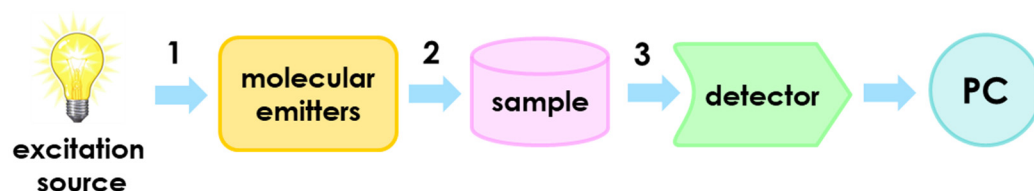

Figure 2. Block diagram of the experimental setup, where 1—exciting light; 2—emitted light; 3—transmitted light.

In order to compare Ir(III) and Cu(I) compounds as a light source in OMS, the series of colored aqueous solutions of copper and cobalt nitrates were chosen because these solutions absorb the light in the visible range ($Co(NO_3)_2$ in the range of 400–600 nm, $Cu(NO_3)_2$—700–900 nm). Individual PLS models were built to relate the registered optical signals with copper and cobalt content, and the respective modeling statistics are presented in Table 1. Despite the simplicity of the developed analytical platform, PLS models for copper and cobalt exhibit a good performance for both OMSs (with Ir(III) and Cu(I) complexes). The parameters of the model for copper quantification are somewhat worse in Cu(I)-based OMS than in Ir(III)-based OMS, while for the cobalt model they are better. A set of copper(I)-based molecular emitters was chosen for further research because it is more efficient both economically and environmentally.

At the next stage, the laser diode was replaced by a UV flashlight. The experimental results showed that the recorded optical density of the initial emission of Cu(I) complexes upon excitation with the UV flashlight is much higher than that upon the laser diode. The PLS results for OMS with UV flashlight are better for both Cu and Co models (Table 1).

Table 1. PLS modeling and validation statistics.

Emission Source	Light Source	Calibration		CV	
		RMSE	R^2	RMSE	R^2
Co [a]	Laser (365 nm)	Ir(III) complexes [c]	0.005	0.98	0.009	0.94
Co [b]	Laser (385 nm)	Cu(I) complexes [d]	0.002	1	0.005	0.98
Co [b]	UV-flashlight	Cu(I) complexes [d]	0.002	0.99	0.004	0.99
Cu [a]	Laser (365 nm)	Ir(III) complexes [c]	0.002	1	0.003	0.99
Cu [b]	Laser (385 nm)	Cu(I) complexes [d]	0.006	0.96	0.013	0.84
Cu [b]	UV-flashlight	Cu(I) complexes [d]	0.003	0.99	0.004	0.98
PO_4^{3-}	UV-flashlight	Cu(I) complex (9)	0.006	1	0.031	0.99
F^-	UV-flashlight	Cu(I) complex (10)	0.020	0.97	0.029	0.96

[a] 7 samples, [b] 10 samples, [c] mixture of 8 Ir(III) complexes, [d] mixture of 6 Cu(I) complexes. The interval range for the modeling: 450–800 nm for Co, Cu, and F^-, 600–750 nm for PO_4^{3-}.

The practical application of the developed Cu(I)-based OMS was demonstrated for the determination of fluoride and phosphate content in real surface and tap waters. Fluoride and phosphate are essential components for living cells; however, excess concentrations in surface water can lead to various human diseases and a general reduction in water quality. The evaluation of fluoride and phosphate by simple and inexpensive analytical methods is an important task for timely environmental monitoring.

The colored complexes of fluoride and phosphate absorb light in the regions of 450–800 (absorption maximum at around 590 nm) and 550–800 nm (absorption maximum at around 700 nm), respectively. Since these analytes are determined using an individual calibration sample set, a single molecular emitter was chosen for each of the anions based on its the emission properties: complex (**9**) with emission maximum of 659 nm for fluoride determination and complex (**10**) with emission maximum of 584 nm for phosphate determination.

The RMSE and R^2 for the full cross-validation are similar for both phosphate and fluoride PLS models (Table 1 and Figure S1 in Supporting Information). Further, the calibration models were used to predict the content of fluoride and phosphate in five water samples. The content of anions evaluated by a standard spectrophotometric technique was employed for model precision assessment. The prediction performance of the phosphate model is pretty good: RMSEP = 0.073 mg/L with R^2 = 0.97. The PLS model for fluoride has also relatively low RMSEP (0.074 mg/L), but R^2 is 0.7. This can be caused by the fact that water samples were taken in different regions and from different sources (several from rivers, one from a lake, and one from a tap). Each sample may contribute strongly to the model, and more samples are needed to make more accurate predictions. Mean squared errors (MSE) that show the average squared difference between the estimated by reference method values and predicted by OMS values were 0.34% and 0.54% for phosphate and fluoride, respectively.

4. Conclusions

The proposed approach to OMS development allows reducing analysis time and does not require additional sample preparation. Moreover, OMS based on molecular emitters can be adopted for the particular analytical task by selecting the appropriate wavelength region. Despite the relative technical simplicity of OMS, its application in combination with modern chemometric methods provides high accuracy of analysis, comparable with that of full-featured spectrometers. Both synthetized sets of Ir(III) and Cu(I)-based complexes are suitable as a light source in OMS. However, Cu(I) complexes are easier to produce, cheaper, and environmentally friendly. The demonstrated application of OMS based on molecular emitters for the determination of fluorides and phosphates in surface water proves their high practical significance.

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